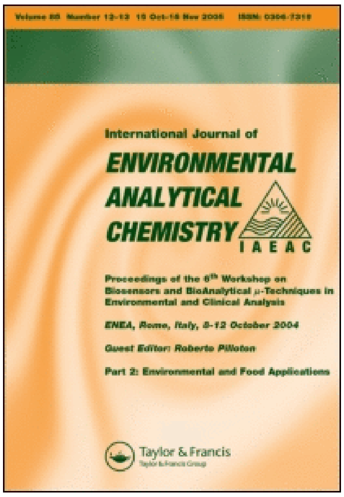

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Albanis, T. A. and Manos, G.(1995) 'Loss of Pendimethalin in Surface Runoff from Plots Untilled and Tilled with Tobacco', International Journal of Environmental Analytical Chemistry, 58: 1, 265 — 273
To link to this Article: DOI: 10.1080/03067319508033129
URL: http://dx.doi.org/10.1080/03067319508033129

Intern. J. Environ. Anal. Chem., Vol. 58, pp. 265-273
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LOSS OF PENDIMETHALIN IN SURFACE RUNOFF FROM PLOTS UNTILLED AND TILLED WITH TOBACCO

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(Received, 10 September 1993; in final form, 25 November 1993)

The loss of pendimethalin (N-(ethylpropyl)-2,6-dinitro-3,4-xylidine), a selective herbicide in runoff water was determined on sandy-clay-loam soil plots cultivated with tobacco in relation with the use of ammonium nitrate limestone as fertelizer, for a period of two years, 1990 and 1991. The surface slope of plots was 11% and the use of fertilizer decreased the soil erosion from a value 617 g/m^2 to 320 g/m^2. The runoff of surface waters were between 16–24% of the rainfall amounts. Reduction in pendimethalin in waterways results from water loss by infiltration, sediment loss, and by attachment adsorption on vegetative and organic matter. Surface runoff levels were highest for the first runoff event after herbicide application, 1.5 g/10 m^2 and initial concentrations were related to the time lapse between herbicide application and the date of the first run-off event. Maximum concentrations were 5.95 and 8.54 µg/L in 1990 and 1991 respectively. Persistence studies showed that pendimethalin concentration in runoff of 0.5 cm soil layer decreased by 88.2%, from 2.46 to 0.29 µg/g within 233 days, in 1990 and by 87.6%, from 2.42 to 0.30 µg/g within 235 days in 1991. After 310 day the concentration of pendimethalin was only 0.1 µg/g.

KEY WORDS: Pendimethalin, runoff, tobacco cultivation, fertilization

INTRODUCTION

Pendimethalin is a dinitroaniline herbicide applied pre-plant incorporated, pre-emergence, pre-transplanting or early post-emergence. It is used for selective control of weeds in crops such as corn (Zea mays L), tobacco (Nicotiana tobacum) soybeans (Glycine max L.Merr.), peas (Pisum satirum L.) winter wheat (Triticum aestivum L.) and several vegetable crops[1–2]. Within the last five years about 90 tons per year of active ingredient of pendimethalin were applied in field in Greece, especially in tobacco cultivations. Comparatively little work has been done on pendimethalin loss from soil, although soil degradation of dinitroaniline herbicides in general has been reviewed[3,4,5].

Pendimethalin can be applied with or without incorporation in soil because it has relatively low volatility (vapor pressure 3×10^{-2} m Hg at 25°C)[2,6]. It is less volatile than trifluralin (α,α,α-trifluro-2,6-dinitro-N,N-dipropyl-p-toluidine) and, fluchloralin (N-(2-chloroethyl)-2-6-dinitro-N-propyl-4-(trifluoromethyl)-aniline)[2,7] and therefore it is lost less rapidly from the soil surface[8]. It was found that pendimethalin is more persistent when incorporated than when applied to the soil surface[9]. More than 60% of the herbicide remained after 5 months when it was incorporated, while only 20% of it remained when incorporation was omitted.

Degradation of pendimethalin proceeds more rapidly under flooded, anaerobic conditions than under aerobic conditions[5,6], which is similar to other dinitroanilines[6,10]. In soil, the 4-methyl group on the benzene ring is oxidized to the carboxylic acid via the corresponding alcohol. The amino nitrogen is also oxidized and the half-life in soil is 3–4 months[2]. Photodecomposition of pendimethalin can occur, although the rate decreases rapidly after the first 7 days of exposure on the soil surface[7,11]. As much as 17% of the applied pendimethalin was lost by photodecomposition within 7 days[11].

Persistence of pendimethalin is influenced by cultivation practices, soil type, temperature and moisture conditions. Walker and Bond (1977) showed that the half-life in a sandy-loam soil was 98 days at 30°C and 409 days at 10°C. At 25°C the half-life increased with decreasing of soil moisture content. In seven different soils there was a trend toward a slower rate of loss as soil organic matter content increased, and the half-life varied from 72 to 172 days[9].

This work presents the results of a 2-year study concerning pendimethalin movement in surface runoff water from small plots of sandy- clay-loam soil on which tobacco was or not grown. The study includes additional determinations of pendimethalin concentration levels and persistence in soil as well as the influence of ammonium nitrate limestone fertilizer on pendimethalin losses.

EXPERIMENTAL PROCEDURE

Experimental design and sample handling

Twelve hydrologically isolated plots were established at the Institute of Technology and Education of Arta (N.W. Greece) to monitor surface water losses. Soil type at the site was a sandy-clay-loam and its composition for two depths 0–30 and 30–60 cm is shown in Table 1. The slope of plots was regulated 11% and a small water-course 1.5 m depth was made in the side with the lower level. The plots were divided and labeled as A, B and C every three

Table 1 Composition of Sandy-clay loam soil for two depths.

	Mechanical Analysis			*Chemical Characteristics*		
Depth	*Sand*[a] %	*Silt*[a] %	*clay*[a] %	*pH*	$CaCO_3$ %	*Organic matter* %
0–30cm	52	18	30	6.1	0.41	1.17
30–60cm	46	28	26	6.4	0	1.20

[a]-Sand, 2.0–0.05 mm; Silt, 0.05–0.002 mm; Clays, below 0.002 mm.

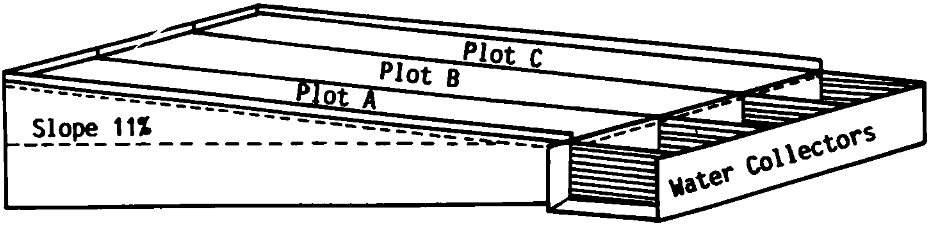

Figure 1 Schematic drawing of experimental plots.

of them (Figure 1). Plot A was cultivated with tobacco and treated with pendimethalin and fertilizer. Plot B was also cultivated with tobacco and treated only with pendimethalin. Plot C, the reference soil, was not cultivated, nor treated with pendimethalin but only with fertilizer.

The plots were separated by a plastic foil of polyethylene 5 mm thick to a depth of 15 cm. The soil was plowed to a depth of 20 cm. A week before the test, all plots were irrigated because of very dry soil conditions.

The soil in the plots was bedded into modified rows in a distance of 45 cm parallel to each other and to the long side of the plots. The plots A and B (Figure 1) were sprayed with pendimethalin formulated as a 350 g/L solution on 10th April 1990 and 14th April 1991 and the application rate was 1.5 Kg/ha. The herbicide was incorporated in the soil to a depth of 5 cm. The removal of herbs in the reference plot C was made twice by hand. Tobacco (Nicotiana Tobaccum S.) was planted on the plots 5 days after herbicide application (15 April 1990 and 21 April 1991). After 30 days, the tobacco was sidedressed at plot A with ammonium nitrate limestone at an application rate of 360 Kg/ha. The soil of the plot C was also treated with the same amount of fertilizer. The tobacco leaves were collected during the season of 10th July to 10th August in both years 1990 and 1991. After harvest, the stalks were chopped and the soil allowed to fallow until the second cultivation.

The first runoff event occurred on October 8th, 1990. The water samples (1 liter) were collected after each runoff event for herbicide analysis. Samples for the major runoff events during the winter were generally collected with an increasing frequency. The amount of soil in the runoff from the plots was filtered and determined. The collected amounts of runoff water and soil as well as the rainfall level between sampling dates are shown in Tables 2 and 3. Soil samples were drawn from each plot, from 16 random cores (5 cm in diameter by 10 cm deep) from a depth 0–15 cm, one day after herbicide application and runoff events.

Extraction and gas chromatography

All the glassware used in the analyses was heated at 250°C for 40 min and repeatedly washed with solvents to remove all the pesticide traces. The solvents used, n-hexane, acetone and benzene were suitable for pesticide residue analysis. Runoff samples were refrigerated at 4°C immediately after collection. Samples were processed in most cases within 1 week after collection.

Table 2 Precipitation and water volume collected after runoff events for the period between April 1990 and March 1991.

Sampling date		Time (days)	Precipitation (mm)	Water Collected in L. Plot A	Plot B	Plot C	Soil Collected in runoff, in g Plot A	Plot B	Plot C
[10 April 1990, application of 1.5 g/10m² pendimethalin]									
30 April	1990	19*	17.5	-	-	-	-	-	-
31 May	1990	50	30.5	-	-	-	-	-	-
30 June	1990	80	10.5	-	-	-	-	-	-
31 July	1990	111	-	-	-	-	-	-	-
31 August	1990	142	13.2	-	-	-	-	-	-
30 September	1990	172	11.4	-	-	-	-	-	-
8 October	1990	181	79.3	3.6	2.7	4.9	23	36	68
11 October	1990	184	208.9	74	70	82	432	795	1,033
8 November	1990	212	214.3	39	42	29.5	223	476	352
29 November	1990	233	37.1	12	11.5	9.	79	138	205
9 December	1990	243	29.0	21.5	20	24.5	120	216	272
28 December	1990	262	42.9	16.2	17.4	19.5	89	201	229
13 February	1991	308	58.0	8.3	6.6	8.4	51	89	98
28 February	1991	323	18.1	-	-	-	-	-	-
31 March	1991	354	45.9	-	-	-	-	-	-
Total			816.6	174.6	170,2	177,8	1,017	1,951	2,257

*The precipitation data correspond to the period between two successive dates.

Table 3 Precipitation and water volume collected after runoff events for the period between April 1991 and May 1992.

Sampling date		Time (days)	Precipitation (mm)	Water Collected in L. Plot A	Plot B	Plot C	Soil Collected in runoff, in g Plot A	Plot B	Plot C
[14 April	*1991, application of 1.5 g/10m²-pendimethalin]*								
17 April	1991	3	134.4	7.5	6.4	5.9	36	35	53
30 April	1991	16	20.3	-	-	-	-	-	-
31 May	1991	47	30.6	-	-	-	-	-	-
30 June	1991	77	10.5	-	-	-	-	-	-
31 July	1991	108	3.6	-	-	-	-	-	-
31 August	1991	139	11.5	-	-	-	-	-	-
30 September	1991	169	13.2	-	-	-	-	-	-
30 October	1991	199	273.3	12.2	15.4	10.5	52	76	63
19 November	1991	219	108.9	19.5	20	22	45	90	115
5 December	1991	235	118.5	22	27.5	26	54	122	130
7 December	1991	236	88.9	206	190	205	396	825	922
11 December	1991	240	63.0	157	162	145	378	850	724
15 December	1991	244	133.5	332	325	340	794	1434	1618
27 December	1991	257	41.1	90	86	97	216	425	470
7 February	1992	299	92.9	12.5	15.1	14.5	32	78	74
19 February	1992	311	130.7	27	25	21	82	127	116
29 March	1992	349	72.8	10	13	9.5	43	79	88
14 April	1992	365	92.1	5.5	4.2	3.7	31	38	24
4 May	1992	385	88.9	2.4	4.2	5.6	15	44	29
Total			1528.7	903.6	893.8	906.7	2,183	4,223	4,416

Water extraction The 1 L unfiltered runoff sample was analyzed by method as described by Lee and Chau (1983)[12]. The sample was acidified with H_2SO_4 1:1 (v/v) until pH~2 and extracted three times with 50 ml portions of dichloromethane. The combined organic extracts were shaken in a separatory funnel with 100 ml 2% $KHCO_3$. The extracts were dried through sintered glass funnel containing 80 g anhydrous sodium sulfate and 3 ml isooctane was added. The final extract was evaporated to ca 10 ml on a rotary evaporator, 50 ml hexane were added and the evaporation was carefully repeated to 4–5 ml.

Soil Extraction A 25g sample of soil was treated as described by Zimdahl *et al.* (1984). This method includes addition of 250 ml of acidified methanol (2% HCl, v/v) and the mixture was shaken for 24 hrs on a reciprocating shaker. After the soil settled, the supernatant was filtered under vacuum and 100 to 150 ml were collected. In a 50 ml portion of the filtrate was added 50 ml n-hexane twice. The aqueous layer was discarded and the hexane layers were combined and evaporated to dryness.

Column chromatography. The concentrated extract were cleaned up by a column 1 cm i.d. containing 6 ml Florisil (6% H_2O, w/v) and 1 ml anhydrous sodium sulfate. The column was rinsed with 30 ml n-hexane, drained and discarded. Pendimethalin was eluted from column with 100 ml of benzene:hexane (20:80 v/v)[5]. The elute was evaporated to dryness and taken up in 0.1 ml of n-hexane for gas-liquid chromatographic analysis.

Gas chromatographic analyses were carried out on a Varian-3300 G.C. fitted with a Ni^{63} E.C. Detector and a glass column 1.8 m long, packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 chromosorb W. Nitrogen was used as the carrier gas at 45 ml/min. The temperatures of the column, injector and detector were 200, 240 and 300°C respectively. All samples were run in triplicate at 2.5 μl injection value. The minimum detection limit was 0.22 μg/L for water samples and 5 μg/Kg for soil samples.

RESULTS AND DISCUSSION

Tables 2 and 3 show rainfall and runoff for two cultivation periods, the first from April 10th, 1990 to March 31st, 1991 and the second from April 14th, 1991 to May 4th, 1992. The rain required for runoff events depended on the season and the time distance between the events. The amounts of runoff were between 0.33 to 25.7% of the rainfall amounts. After a dry period, about 80 mm of rainfall was required for the first runoff event in 8th October 1990 and the collected amount of water was very low 2.7–4.9 L. During the winter smaller amount of rainfall were required to have runoff events with higher amounts of collected water. The same behaviour was observed during 1991, when in 17th April and 30th October, 134.4 and 273.3 mm of rainfall was required for runoff amounts of 5.9–7.5 and 10.5–15.4L respectively. The runoff was extremely higher during December 1991.

The use of ammonium nitrate limestone as fertilizer in a rate of 360 Kg/ha decreased the soil erosion in the runoff water from a value of 617 g/m^2 in plot B without fertilizer treatment, and 667 g/m^2 in plot C without pendimethalin and fertilizer treatment to 320 g/m^2 in plot A, where fertilizer used. The results obtained by the procedure described above from soil and

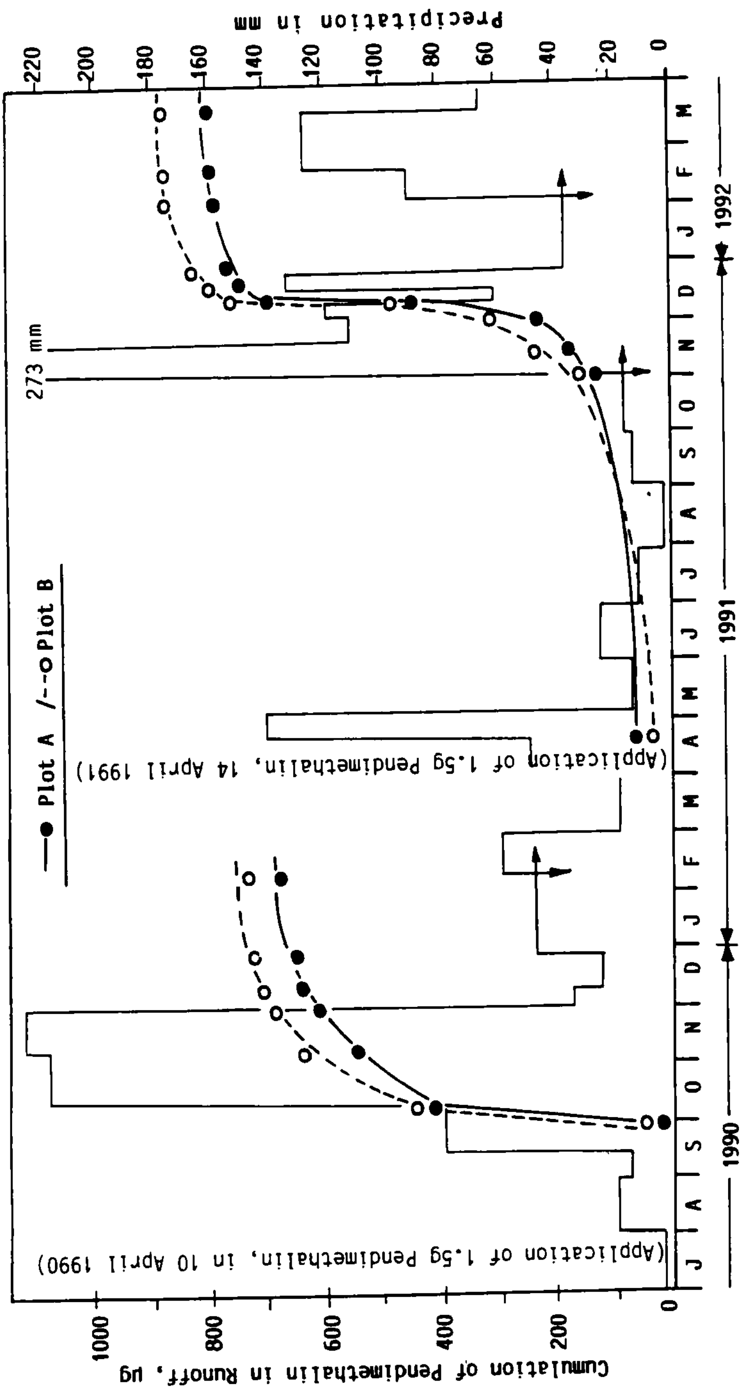

Figure 2 Loss of pendimethalin in runoff plots with (A) and without (B) fertilizer treatment, as a function of rainfall.

Table 4 Pendimethalin in runoff water collected and its *corresponding concentrations in* soil of plots, between April 10, 1990 and May 4, 1992 (N = 3).

	Plot A			*Plot B*		
Time (days)	*Concentr. Soil (μg/g)*	*Concentr. runoff (μg/L)*	*C'tive amount (μg)*	*Concentr. soil (μg/g)*	*Concentr. runoff (μg/L)*	*C'tive amount (μg)*
0	[10 April 1990, application of 1.5 kg/ha pendimethalin]					
4	2.26	—	—	2.18	—	—
181	0.45	2.46	8.8	0.41	3.16	8.5
184	0.42	5.54	418.7	0.43	5.95	425.0
212	0.35	4.12	579.4	0.28	5.21	643.8
233	0.29	3.12	616.8	0.18	3.26	681.3
243	0.20	1.35	645.8	0.15	1.87	718.7
262	0.17	0.12	647.7	0.14	0.31	724.1
308	0.11	0.24	649.9	0.09	0.17	725.2
0	[14 April 1991, application of 1.5 Kg/ha pendimethalin]					
3	2.42	8.72	65.4	2.43	8.54	54.6
199	0.53	4.65	122.1	0.49	7.14	164.5
219	0.48	3.44	189.2	0.38	4.60	256.5
235	0.36	2.10	235.4	0.35	1.88	308.2
236	0.34	1.12	466.1	0.29	0.95	488.7
240	0.28	1.63	722.0	0.23	1.87	791.6
244	0.30	0.14	768.5	0.26	0.22	863.1
257	0.23	0.09	776.6	0.17	0.11	872.6
299	0.14	0.27	779.9	0.12	0.09	873.9
311	0.10	0.15	783.9	0.10	0.04	874.9
349	0.05	0.02	784.1	n.d.	0.03	875.3
365	n.d.[a]	n.d.	—	n.d.	n.d.	—
385	n.d.	n.d.	—	n.d.	n.d.	—

[a]. Not detected

water samples of plots A and B where the tobacco was cultivated, as well as the reference soil plot C are shown in Table 4 and Figure 2. Each year the concentration was higher in the first surface runoff event following pendimethalin application to the tobacco crop. Thereafter the levels of the herbicide were generally decreasing with subsequent runoff events. Samples taken during winter and early spring often showed very low pendimethalin levels of 1μg/L or less.

The maximum pendimethalin concentrations in surface runoff during the two year study period was 5.95 and 8.54 μg/L in 1990 and 1991 respectively. The first runoff in 1990 took place 181 days after herbicide application and the first runoff of 1991 only 3 days after herbicide application. The first year 1990, there was a large time lapse from April to October between herbicide application and the first runoff event. In the second year 1991 although a rainfall event took place just three days after pendimethalin application, the second runoff event took also place next October. In the mean time the applied pendimethalin was subjected to degradation. The data showed a relationship between the time lapse between pendimethalin application and the first rainfall event on one hand and the herbicide concentrations in the first (1990) and second (1991) runoff event.

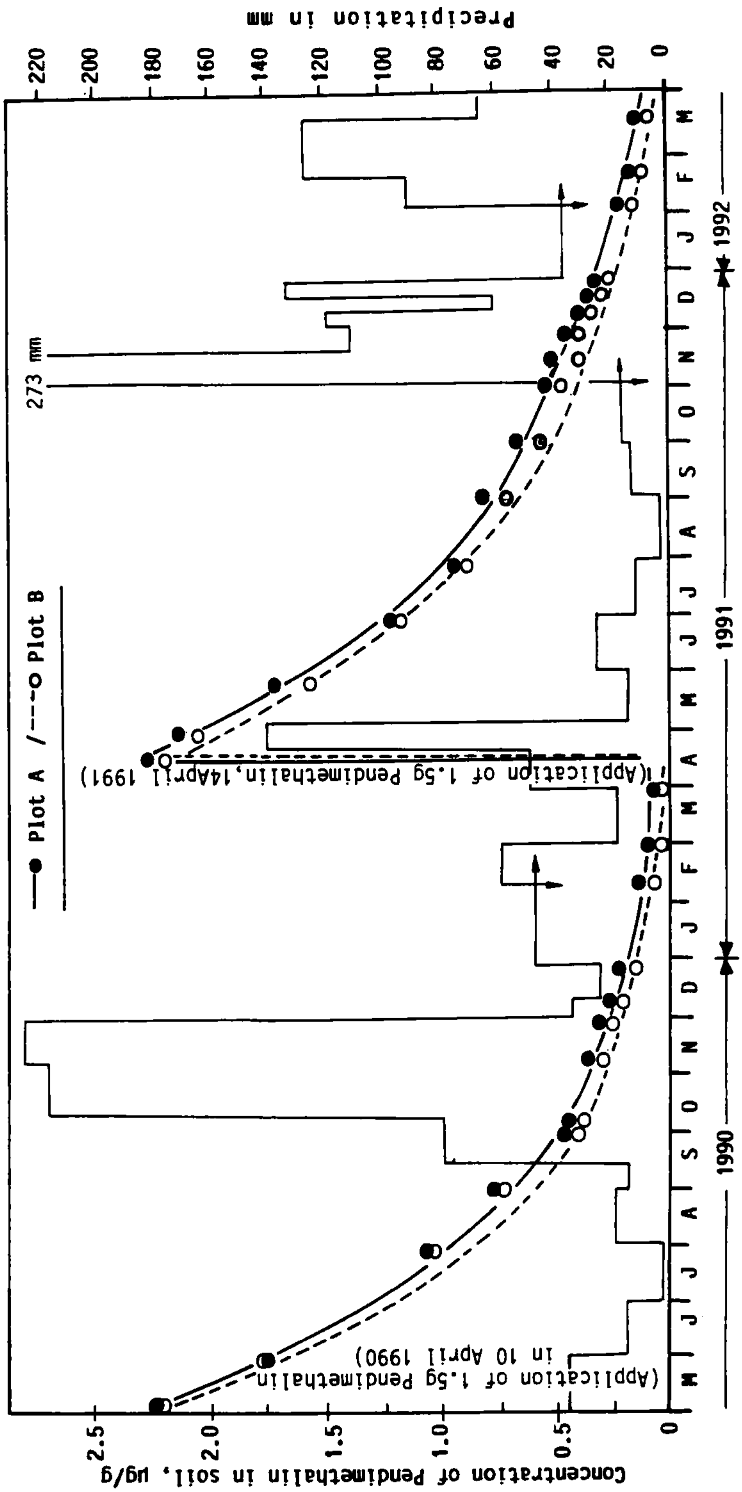

Figure 3 Residue concentrations of pendimethalin in soil with (A) and without (B) fertilizer treatment.

The results obtained from soil samples, of the plots A and B where the tobacco was cultivated are shown in Figure 3. This figure summarizes the changes in pendimethalin residue concentrations for the period between April 10th, 1990 and May 4th, 1992. It also contains the amount of rainfall. Pendimethalin in the first cultivation period, in soil of the plot A with fertilizer treatment, had a half life 97 days and in plot B without fertilizer had a half life decreased to 88 days. The half life of pendimethalin in the second cultivation period, in soil of plot A, with fertilizer treatment was 90 days and without fertilizer (plot B), it was decreased to 84 days.

More detailed information from the watersheds is given in Figure 2, which shows rainfall, pendimethalin cumulative runoff and persistence of pendimethalin in the soil surface, 0–0.5 cm. These results show that most of the applied pendimethalin had dissipated before the first runoff event. To be more precise, 181 days after the herbicide was applied the soil concentration was only 0.43 μg/g in 1990, a 82.8% decrease from the initial level. By the first runoff event in autumn of 1991, 199 days after the herbicide application, the soil concentration was only 0.51 μg/g, a 79% decrease from the initial level.

The overall results from these watershed studies under natural rainfall conditions, indicated that there was little movement of pendimethalin in surface flow. Losses of pendimethalin in surface runoff, resulting from naturals rains on the plots, were estimated at only 0.043 and 0.048% of that applied in plot A and B respectively in the first cultivation period (1990–1991) and 0.052 and 0.058% in the second period (1991–1992). The extent of pendimethalin leaching seemed to vary from year to year. Since all other conditions were held constant, weather variables, especially rainfall, is assumed to be responsible for the observed differences. We consider that the robust tobacco plants in plot A treated with fertilizer, as compared with the plants in plot B, protected the soil from erosion and intercepted or absorbed the greater portion of pendimethalin.

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